

Claims

1. A positive bottom photoimageable antireflective coating composition which is capable of being developed in an aqueous alkaline developer and which is coated below a positive photoresist, where the antireflective coating composition comprises a photoacid generator and a polymer comprising at least one unit with an acid labile group and at least one unit with an absorbing chromophore.

2. The composition according to claim 1 where the acid labile group is selected from $-(CO)O-R$, $-O-R$, $-O(CO)O-R$, $-C(CF_3)_2O-R$, $-C(CF_3)_2O(CO)O-R$ and $-C(CF_3)_2(COOR)$, where R is alkyl, cycloalkyl, substituted cycloalkyl, oxocyclohexyl, cyclic lactone, benzyl, substituted benzyl, alkoxy alkyl, acetoxo alkoxyoxy alkyl, tetrahydrofuranyl, methyl adamantyl, menthyl, tetrahydropyranyl and mevalonic lactone.

3. The composition according to claim 1 where the absorbing chromophore is selected from compounds containing hydrocarbon aromatic rings, substituted and unsubstituted phenyl, substituted and unsubstituted anthracyl, substituted and unsubstituted phenanthryl, substituted and unsubstituted naphthyl, substituted and unsubstituted heterocyclic aromatic rings containing heteroatoms selected from oxygen, nitrogen, sulfur, or combinations thereof.

4. The composition according to claim 1 where the acid labile group and the absorbing chromophore are in the same unit.

5. The composition according to claim 1 where the polymer is selected from copolymers of 2-methyl-2-adamantyl methacrylate, mevalonic lactone methacrylate, 3-hydroxy-1-adamantyl methacrylate, methacrylate ester of beta-hydroxy-gamma-butyrolactone, t-butyl nornyl carboxylate, t-butyl methyl adamantyl methacrylate, t-butyl acrylate and t-butyl methacrylate; t-butoxy carbonyl oxy vinyl benzene, benzyl oxy carbonyl oxy vinyl benzene; ethoxy ethyl oxy vinyl benzene; trimethyl silyl ether of vinyl phenol, and 2-tris(trimethylsilyl)silyl ethyl ester of methyl methacrylate, with acrylic acid, methacrylic acid, vinyl alcohol, maleic

anhydride, maleic acid, maleimide, N-methyl maleimide, N-hydroxymethyl acrylamide, N-vinyl pyrrolidinone, methyl methacrylate, butyl methacrylate, hydroxyethyl methacrylate and hydroxypropyl methacrylate, hydroxystyrene, styrene, acetoxystyrene, benzyl methacrylate, N-methyl maleimide, vinyl benzoate, vinyl 4-tert-butylbenzoate, ethylene glycol phenyl ether acrylate, phenoxypropyl acrylate, 2-hydroxy-3-phenoxypropyl acrylate, phenyl methacrylate, benzyl methacrylate, 9-anthracenylmethyl methacrylate, 9-vinylnanthracene, 2-vinylnaphthalene, N-vinylphthalimide, N-(3-hydroxy)phenyl methacrylamide, N-(3-hydroxy-4-hydroxycarbonylphenylazo)phenyl methacrylamide, N-(3-hydroxyl-4-ethoxycarbonylphenylazo)phenyl methacrylamide, N-(2,4-dinitrophenylaminophenyl) maleimide, 3-(4-acetoaminophenyl)azo-4-hydroxystyrene, 3-(4-ethoxycarbonylphenyl)azo-acetoacetoxy ethyl methacrylate, 3-(4-hydroxyphenyl)azo-acetoacetoxy ethyl methacrylate, tetrahydroammonium sulfate salt of 3-(4-sulfophenyl)azoacetoacetoxy ethyl methacrylate.

6. The composition according to claim 1 where the antireflective layer has a k value in the range of 0.1 to 1.0.

7. The composition according to claim 1 where the antireflective layer has a thickness less than the thickness of the photoresist.

8. The composition according to claim 1 where the photoacid generator is sensitive in the range of 450 nm to 100 nm.

9. The composition according to claim 8 where the photoacid generator is sensitive at wavelengths selected from 436 nm, 365 nm, 248 nm, 193 nm and 157 nm.

10. The composition according to claim 1 where the antireflective coating is substantially insoluble in a solvent of the top photoresist.

11. A process for forming a positive image comprising:

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- a) providing a coating of the bottom photoimageable antireflective coating composition of claim 1 on a substrate;
 - b) providing a coating of a top photoresist layer over the bottom coating;
 - c) imagewise exposing the top and bottom layers to actinic radiation of same wavelength;
 - d) postexposure baking the substrate; and,
 - e) developing the top and bottom layers with an aqueous alkaline solution.

10 12. The process according to claim 11 where the antireflective coating is insoluble in the aqueous alkaline solution prior to the exposing step and becomes soluble prior to the developing step.

15 13. The process according to claim 11 where the aqueous alkaline solution comprises tetramethylammonium hydroxide.

14. The process according to claim 13 where the aqueous alkaline solution further comprises a surfactant.

20 15. A positive bottom photoimageable antireflective coating composition which is capable of being developed in an aqueous alkaline developer and which is coated below a positive photoresist, where the antireflective coating composition comprises a photoacid generator, a dye and a polymer comprising at least one unit with an acid labile group.

25 16. The composition according to claim 15 where the dye is selected from a monomeric dye, a polymeric dye and a mixture of a monomeric and a polymeric dyes.

30 17. The composition according to claim 15 where the dye is selected from compounds containing substituted and unsubstituted phenyl, substituted and unsubstituted anthracyl, substituted and unsubstituted phenanthryl, substituted and unsubstituted naphthyl, substituted and unsubstituted heterocyclic aromatic

rings containing heteroatoms selected from oxygen, nitrogen, sulfur, or combinations thereof.

18. The composition according to claim 15 where the acid labile group is selected from $-(CO)O-R$, $-O-R$, $-O(CO)O-R$, $-C(CF_3)_2O-R$, $-C(CF_3)_2O(CO)O-R$ and $-C(CF_3)_2(COOR)$, where R is alkyl, cycloalkyl, substituted cycloalkyl, oxocyclohexyl, cyclic lactone, benzyl, substituted benzyl, alkoxy alkyl, acetoxy alkoxyoxy alkyl, tetrahydrofuranyl, methyl adamantyl, menthyl, tetrahydropyranyl and mevalonic lactone.

19. The composition according to claim 15 where the polymer is selected from copolymers of 2-methyl-2-adamantyl methacrylate, mevalonic lactone methacrylate, 3-hydroxy-1-adamantyl methacrylate, methacrylate ester of beta-hydroxy-gamma-butyrolactone, t-butyl norbornyl carboxylate, t-butyl methyl adamantyl methacrylate, methyl adamantyl acrylate, t-butyl acrylate and t-butyl methacrylate; t-butoxy carbonyl oxy vinyl benzene, benzyl oxy carbonyl oxy vinyl benzene; ethoxy ethyl oxy vinyl benzene; trimethyl silyl ether of vinyl phenol, and 2-tris(trimethylsilyl)silyl ethyl ester of methyl methacrylate, with acrylic acid, methacrylic acid, vinyl alcohol, maleic anhydride, maleic acid, maleimide, N-methyl maleimide, N-hydroxymethyl acrylamide, N-vinyl pyrrolidinone, methyl methacrylate, butyl methacrylate, hydroxyethyl methacrylate and hydroxypropyl methacrylate.

20. The composition according to claim 15 where the antireflective layer has a k value in the range of 0.1 to 1.0.

21. The composition according to claim 15 where the antireflective layer has a thickness less than the thickness of the photoresist.

22. The composition according to claim 15 where the photoacid generator is sensitive in the range of 450 nm to 100 nm.



23. The composition according to claim 15 where the photoacid generator is sensitive to wavelengths selected from 436 nm, 365 nm, 248 nm, 193 nm and 157 nm.

5 24. The composition according to claim 15 where the antireflective coating is substantially insoluble in a solvent of the top photoresist.

25. A process for forming a positive image comprising:

- 10 a) providing a coating of the bottom photoimageable antireflective coating composition of claim 15 on a substrate;
- b) providing a coating of a top photoresist layer above the bottom coating;
- c) imagewise exposing the top and bottom layers to actinic radiation of same wavelength;
- 15 d) postexposure baking the substrate; and,
- e) developing the top and bottom layers with an aqueous alkaline solution.

20 26. The process according to claim 25 where the antireflective coating is insoluble in the aqueous alkaline solution prior to exposing step and becomes soluble prior to the developing step.

25 27. The process according to claim 25 where the aqueous alkaline solution comprises tetramethylammonium hydroxide.

28. The process according to claim 27 where the aqueous alkaline solution further comprises a surfactant.

30 29. A positive bottom photoimageable antireflective coating composition which is capable of being developed in an aqueous alkaline developer and which is coated below a positive photoresist, where the antireflective coating composition comprises a polymer comprising at least one unit with an acid labile group.

30. The composition according to claim 29 where the acid labile group is selected from $-(CO)O-R$, $-O-R$, $-O(CO)O-R$, $-C(CF_3)_2O-R$, $-C(CF_3)_2O(CO)O-R$ and $-C(CF_3)_2(COOR)$, where R is alkyl, cycloalkyl, substituted cycloalkyl, oxocyclohexyl, cyclic lactone, benzyl, substituted benzyl, alkoxy alkyl, acetoxymethoxy alkyl, tetrahydrofuranyl, methyl adamantyl, menthyl, tetrahydropyranyl and mevalonic lactone.

31. The composition according to claim 29 where the polymer further contains an absorbing chromophore.

32. The composition according to claim 29 where the polymer is selected from 2-methyl-2-adamantyl methacrylate, mevalonic lactone methacrylate, t-butyl norbornyl carboxylate, 3-hydroxy-1-adamantyl methacrylate, methacrylate ester of beta-hydroxy-gama-butyrolactone, t-butyl methyl adamantyl methacrylate, methyl adamantyl acrylate, t-butyl acrylate and t-butyl methacrylate; t-butoxy carbonyl oxy vinyl benzene, benzyl oxy carbonyl oxy vinyl benzene; ethoxy ethyl oxy vinyl benzene; trimethyl silyl ether of vinyl phenol, and 2-tris(trimethylsilyl)silyl ethyl ester of methyl methacrylate, with acrylic acid, methacrylic acid, vinyl alcohol, maleic anhydride, maleic acid, maleimide, N-methyl maleimide, N-hydroxymethyl acrylamide, N-vinyl pyrrolidinone, methyl methacrylate, butyl methacrylate, hydroxyethyl methacrylate and hydroxypropyl methacrylate, hydroxystyrene, styrene, acetoxystyrene, benzyl methacrylate, N-methyl maleimide, vinyl benzoate, vinyl 4-tert-butylbenzoate, ethylene glycol phenyl ether acrylate, phenoxypropyl acrylate, 2-hydroxy-3-phenoxypropyl acrylate, phenyl methacrylate, benzyl methacrylate, 9-anthracenylmethyl methacrylate, 9-vinylanthracene, 2-vinylnaphthalene, N-vinylphthalimide, N-(3-hydroxy)phenyl methacrylamide, N-(3-hydroxy-4-hydroxycarbonylphenylazo)phenyl methacrylamide, N-(3-hydroxy-4-ethoxycarbonylphenylazo)phenyl methacrylamide, N-(2,4-dinitrophenylaminophenyl) maleimide, 3-(4-acetoaminophenyl)azo-4-hydroxystyrene, 3-(4-ethoxycarbonylphenyl)azo-acetoacetoxy ethyl methacrylate, 3-(4-hydroxyphenyl)azo-acetoacetoxy ethyl methacrylate, tetrahydroammonium sulfate salt of 3-(4-sulfophenyl)azoacetoacetoxy ethyl methacrylate.

33. The composition according to claim 29 further comprising a dye.

34. The composition according to claim 33 where the dye is selected from a monomeric dye, a polymeric dye and a mixture of a monomeric and a polymeric dyes.

35. The composition according to claim 29 where the antireflective layer has a k value in the range of 0.1 to 1.0.

36. A composition according to claim 29 where the antireflective layer has a thickness less than the thickness of the photoresist.

37. The composition according to claim 29 where the antireflective coating is substantially insoluble in a solvent of the top photoresist.

38. A process for forming a positive image comprising:

- a) providing a coating of the bottom photoimageable antireflective coating composition of claim 29 on a substrate;
- b) providing a coating of a top photoresist layer above the bottom coating;
- c) imagewise exposing the top and bottom layers to actinic radiation of same wavelength;
- d) postexposure baking the substrate, and thereby diffusing acid from the photoresist into the antireflective coating; and,
- e) developing the top and bottom layers with an aqueous alkaline solution.

39. The process according to claim 38 where the antireflective coating is insoluble in the aqueous alkaline solution prior to exposing step and becomes soluble prior to the developing step.

40. The process according to claim 38 where the aqueous alkaline solution comprises tetramethylammonium hydroxide.

41. The process according to claim 40 where the aqueous alkaline solution further comprises a surfactant.

5 42. A process for forming a positive image comprising;

- a) providing a coating of a bottom photoimageable and alkali developable antireflective coating composition on a substrate;
- b) providing a coating of a top photoresist layer;
- c) imagewise exposing the top and bottom layer to actinic radiation of same wavelength;
- d) postexposure baking the substrate; and,
- e) developing the top and bottom layer with an aqueous alkaline solution.

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43. The process according to claim 42 where the antireflective coating is insoluble in the alkaline solution prior to exposure step and becomes soluble prior to the developing step.

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44. The process according to claim 42 where the antireflective coating comprises a polymer and a photoacid generator.

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45. The process according to claim 42 where the polymer comprises an acid labile group.

46. The process according to claim 45, where the polymer further comprises an absorbing chromophore.

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47. The process according to claim 44, where the antireflective coating further comprises a dye.